Appendix 6 Derivation of the Higher-Order Density Matrix Elements for Doublet and Triplet Electronic Levels

A6.1 Doublet Electronic Levels

Rotational Energy: Second-Order Correction for Centrifugal Distortion

$$\frac{H_{11R}}{B_v}=F_{11R}=z+\Lambda \quad F_{22R}=z-\Lambda \quad F_{12R}=F_{21R}=-\left(z-\Lambda^2\right)^{1/2}$$
$$\frac{H_{11CD}}{-D_v}=F_{11CD}=z^2+(1+2\Lambda)z,\ F_{22CD}=z^2+(1-2\Lambda)z,$$
$$F_{12CD}=F_{21CD}=-2z\left(z-\Lambda^2\right)^{1/2}$$

$$H_{11CH}=\frac{1}{2}H_v\left[(F_{CD}F_R)_{11}+(F_RF_{CD})_{11}\right]=H_v(F_{SR}F_R)_{11}=H_v(F_{11CD}F_{11R}+F_{12CD}F_{21R})$$
$$=H_v\left\{\left[z^2+(1+2\Lambda)z\right](z+\Lambda)+2z\left(z-\Lambda^2\right)\right\}=H_v\left[z^3+(3+3\Lambda)z^2+\Lambda z\right]$$

$$H_{22CH}=\frac{1}{2}H_v\left[(F_{CD}F_R)_{22}+(F_RF_{CD})_{22}\right]=H_v(F_{CD}F_R)_{22}=H_v(F_{22CD}F_{22R}+F_{21CD}F_{12R})$$
$$=H_v\left\{\left[z^2+(1-2\Lambda)z\right](z-\Lambda)+2z\left(z-\Lambda^2\right)\right\}=H_v\left[z^3+(3-3\Lambda)z^2-\Lambda z\right]$$

$$H_{12CH}=\frac{1}{2}H_v(F_{12CD}F_{22R}+F_{11CD}F_{12R}+F_{12R}F_{22CD}+F_{11R}F_{12CD})$$
$$=\frac{1}{2}H_v\left(z-\Lambda^2\right)^{1/2}\left\{-2z(z-\Lambda)-\left[z^2+(1+2\Lambda)z\right]-\left[z^2+(1-2\Lambda)z\right]-2z(z+\Lambda)\right\}$$
$$=-H_v\left(z-\Lambda^2\right)^{1/2}\left[3z^2+z\right].$$

(A6.1)

Rotational Energy: Third -Order Correction for Centrifugal Distortion

$$\frac{H_{11R}}{B_v}=F_{11R}=z+\Lambda \quad F_{22R}=z-\Lambda \quad F_{12R}=F_{21R}=-\left(z-\Lambda^2\right)^{1/2}$$
$$\frac{H_{11CH}}{-D_v}=F_{11CD}=z^3+(3+3\Lambda)z^2+\Lambda z,\ F_{22CH}=z^3+(3-3\Lambda)z^2-\Lambda z,$$
$$F_{12CH}=F_{21CH}=-\left(z-\Lambda^2\right)^{1/2}\left(3z^2+z\right)$$

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$$
\begin{aligned}
H_{11CL} &= -\frac{1}{2}L_v\left[(F_{CH}F_R)_{11} + (F_RF_{CH})_{11}\right] = -L_v(F_{CH}F_R)_{11} \\
&= -L_v(F_{11CH}F_{11R} + F_{12CH}F_{21R}) \\
&= -L_v\left\{\left[z^3 + (3+3\Lambda)z^2 + \Lambda z\right](z+\Lambda) + \left(3z^2+z\right)\left(z-\Lambda^2\right)\right\} \\
&= -L_v\left[z^4 + (6+3\Lambda)z^3 + (1+4\Lambda)z^2\right]
\end{aligned}
$$

$$
\begin{aligned}
H_{22CL} &= -\frac{1}{2}L_v\left[(F_{CH}F_R)_{22} + (F_RF_{CH})_{22}\right] = -L_v(F_{CH}F_R)_{22} \\
&= -L_v(F_{22CH}F_{22R} + F_{21CH}F_{12R}) \\
&= -L_v\left\{\left[z^3 + (3+3\Lambda)z^2 - \Lambda z\right](z-\Lambda) + \left(3z^2+z\right)\left(z-\Lambda^2\right)\right\} \\
&= -L_v\left[z^4 + (6+3\Lambda)z^3 + \left(1+3\Lambda-7\Lambda^2\right)z^2\right]
\end{aligned}
$$

$$
\begin{aligned}
H_{12CL} &= -\frac{1}{2}L_v\left[(F_{CH}F_R)_{12} + (F_RF_{CH})_{12}\right] \\
&= -\frac{1}{2}L_v(F_{11CH}F_{12R} + F_{12CH}F_{22R} + F_{11R}F_{12CH} + F_{12R}F_{22CH}) \\
&= -\frac{1}{2}L_v\left(z-\Lambda^2\right)^{1/2}\left\{-\left[z^3 + (3+3\Lambda)z^2 + \Lambda z\right] - \left(3z^2+z\right)(z-\Lambda)\right\} \\
&\quad -\frac{1}{2}L_v\left(z-\Lambda^2\right)^{1/2}\left\{-(z+\Lambda)\left(3z^2+z\right) - \left[z^3 + (3-3\Lambda)z^2 - \Lambda z\right]\right\} \\
&= L_v\left(z-\Lambda^2\right)^{1/2}\left[4z^3 + 4z^2\right].
\end{aligned}
\tag{A6.2}
$$

Spin–Rotation Interaction: First-Order Correction for Centrifugal Distortion

$$
\begin{aligned}
&\frac{H_{11R}}{B_v} = F_{11R} = z+\Lambda \quad F_{22R} = z-\Lambda \quad F_{12R} = F_{21R} = -\left(z-\Lambda^2\right)^{1/2} \\
&\frac{H_{11SR}}{\gamma_v} = F_{11SR} = -\frac{1}{2}(\Lambda+1) \quad F_{22SR} = \frac{1}{2}(\Lambda-1) \quad F_{12SR} = F_{21SR} = \frac{1}{2}\left(z-\Lambda^2\right)^{1/2} \\
&H_{11SRD} = \frac{1}{2}\gamma_{Dv}\left[(F_{SR}F_R)_{11} + (F_RF_{SR})_{11}\right] = \gamma_{Dv}(F_{11SR}F_{11R} + F_{12SR}F_{21R}) \\
&\qquad = \gamma_{Dv}\left[-\frac{1}{2}(\Lambda+1)(z+\Lambda) - \frac{1}{2}\left(z-\Lambda^2\right)\right] = -\frac{1}{2}\gamma_{Dv}(2z + \Lambda z + \Lambda) \\
&H_{22SRD} = \frac{1}{2}\gamma_{Dv}\left[(F_{SR}F_R)_{22} + (F_RF_{SR})_{22}\right] = \gamma_{Dv}(F_{22SR}F_{22R} + F_{21SR}F_{12R}) \\
&\qquad = \gamma_{Dv}\left[\frac{1}{2}(\Lambda-1)(z-\Lambda) - \frac{1}{2}\left(z-\Lambda^2\right)\right] = \frac{1}{2}\gamma_{Dv}(-2z + z\Lambda + \Lambda) \\
&H_{12SRD} = \frac{1}{2}\gamma_{Dv}(F_{12SR}F_{22R} + F_{11SR}F_{12R} + F_{12R}F_{22SR} + F_{11R}F_{12SR}) \\
&\qquad = \frac{1}{2}\gamma_{Dv}\left(z-\Lambda^2\right)^{1/2}\left[\frac{1}{2}(z-\Lambda) + \frac{1}{2}(\Lambda+1) - \frac{1}{2}(\Lambda-1) + \frac{1}{2}(z+\Lambda)\right] \\
&\qquad = \frac{1}{2}\gamma_{Dv}\left(z-\Lambda^2\right)^{1/2}(z+1)
\end{aligned}
\tag{A6.3}
$$

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Spin–Rotation Interaction: Second-Order Correction for Centrifugal Distortion

$$\frac{H_{11SRD}}{\gamma_v} = F_{11SRD} = -\frac{1}{2}(2z + \Lambda z + \Lambda) \quad F_{22SRD} = \frac{1}{2}(-2z + z\Lambda + \Lambda),$$
$$F_{12SR} = F_{21SR} = \frac{1}{2}\left(z - \Lambda^2\right)^{1/2}(z+1)$$

$$\begin{aligned} H_{11SRH} &= \frac{1}{2}\gamma_{Hv}\left[(F_{SRD}F_R)_{11} + (F_R F_{SRD})_{11}\right] = \gamma_{Hv}(F_{11SRD}F_{11R} + F_{12SRD}F_{21R}) \\ &= \gamma_{Hv}\left[-\frac{1}{2}(2z + \Lambda z + \Lambda)(z + \Lambda) - \frac{1}{2}\left(z - \Lambda^2\right)(z+1)\right] \\ &= -\frac{1}{2}\gamma_{Hv}\left[z^2(3 + \Lambda) + z(1 + 3\Lambda)\right] \end{aligned}$$

$$\begin{aligned} H_{22SRH} &= \frac{1}{2}\gamma_{Hv}\left[(F_{SRD}F_R)_{22} + (F_R F_{SRD})_{22}\right] = \gamma_{Hv}(F_{22SRD}F_{22R} + F_{21SRD}F_{12R}) \\ &= \gamma_{Hv}\left[-\frac{1}{2}(-2z + \Lambda z + \Lambda)(z - \Lambda) - \frac{1}{2}\left(z - \Lambda^2\right)(z+1)\right] \\ &= -\frac{1}{2}\gamma_{Hv}\left[z^2(-1 + \Lambda) + z\left(1 + 3\Lambda - 2\Lambda^2\right) - 2\Lambda^2\right] \end{aligned}$$

$$\begin{aligned} H_{12SRH} &= \frac{1}{2}\gamma_{Hv}(F_{12SRD}F_{22R} + F_{11SRD}F_{12R} + F_{12R}F_{22SRD} + F_{11R}F_{12SRD}) \\ &= \frac{1}{4}\gamma_{Hv}\left(z - \Lambda^2\right)^{1/2}[(z+1)(z - \Lambda) - (2z + \Lambda z + \Lambda) - (-2z + z\Lambda + \Lambda) \\ &\quad + (z + \Lambda)(z+1)] = \frac{1}{2}\gamma_{Hv}\left(z - \Lambda^2\right)^{1/2}\left[z^2 + z(1 - \Lambda) - \Lambda\right]. \end{aligned}$$

(A6.4)

Spin–Orbit Interaction: First-Order Correction for Centrifugal Distortion

$$\frac{H_{11R}}{B_v} = F_{11R} = z + \Lambda \quad F_{22R} = z - \Lambda \quad F_{12R} = F_{21R} = -\left(z - \Lambda^2\right)^{1/2}$$

$$\frac{H_{11SO}}{A_v} = F_{11SO} = -\frac{1}{2}\Lambda \quad F_{22SO} = \frac{1}{2}\Lambda \quad F_{12SO} = F_{21S}) = 0$$

$$H_{11SOD} = \frac{1}{2}A_{Dv}\left[(F_{SO}F_R)_{11} + (F_R F_{SO})_{11}\right] = A_{Dv}F_{11SO}F_{11R} = -\frac{1}{2}A_{Dv}\Lambda(z + \Lambda)$$

$$H_{22SOD} = \frac{1}{2}A_{Dv}\left[(F_{SO}F_R)_{22} + (F_R F_{SO})_{22}\right] = A_{Dv}\left[\frac{1}{2}\Lambda(z - \Lambda)\right] = \frac{1}{2}A_{Dv}\Lambda(z - \Lambda)$$

$$\begin{aligned} H_{12SOD} &= \frac{1}{2}A_{Dv}(F_{12SO}F_{22R} + F_{11SO}F_{12R} + F_{12R}F_{22SO} + F_{11R}F_{12SO}) \\ &= -\frac{1}{2}A_{Dv}\left(z - \Lambda^2\right)^{1/2}\left(-\frac{1}{2}\Lambda + \frac{1}{2}\Lambda\right) = 0. \end{aligned}$$

(A6.5)

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Spin–Orbit Interaction: Second-Order Correction for Centrifugal Distortion

$$
\begin{aligned}
&\frac{H_{11R}}{B_{\mathrm{v}}} = F_{11R} = z + \Lambda \quad F_{22R} = z - \Lambda \quad F_{12R} = F_{21R} = -\left(z - \Lambda^2\right)^{1/2} \\
&\frac{H_{11SOD}}{A_{D\mathrm{v}}} = F_{11SOD} = -\frac{1}{2}\Lambda(z + \Lambda) \quad F_{22SOD} = \frac{1}{2}\Lambda(z - \Lambda) \quad F_{12SOD} = F_{21SOD} = 0 \\
&H_{11SOH} = \frac{1}{2}A_{\mathrm{Hv}}\left[(F_{SOD}F_R)_{11} + (F_RF_{SOD})_{11}\right] = A_{H\mathrm{v}}F_{11SOD}F_{11R} = -\frac{1}{2}A_{H\mathrm{v}}\Lambda(z + \Lambda)^2 \\
&H_{22SOH} = \frac{1}{2}A_{H\mathrm{v}}\left[(F_{SOD}F_R)_{22} + (F_RF_{SOD})_{22}\right] = A_{H\mathrm{v}}F_{22SO}F_{22R} = \frac{1}{2}A_{H\mathrm{v}}\Lambda(z - \Lambda)^2 \\
&H_{12SOH} = \frac{1}{2}A_{\mathrm{Hv}}(F_{12SOD}F_{22R} + F_{11SOD}F_{12R} + F_{12R}F_{22SOD} + F_{11R}F_{12SOD}) \\
&\qquad = \frac{1}{4}A_{H\mathrm{v}}\left(z - \Lambda^2\right)^{1/2}[\Lambda(z + \Lambda) - \Lambda(z - \Lambda)] = \frac{1}{2}A_{H\mathrm{v}}\left(z - \Lambda^2\right)^{1/2}\Lambda^2.
\end{aligned}
\tag{A6.6}
$$

Lambda-Doubling: First-Order Correction for Centrifugal Distortion

$$
\begin{aligned}
&F_{11q\Lambda e/f} = \mp\sqrt{z} \quad F_{12q\Lambda e/f} = \pm\frac{1}{2}\sqrt{z(z-1)} \quad F_{11p\Lambda e/f} = \mp\frac{1}{2}\sqrt{z} \\
&\frac{H_{11R}}{B_{\mathrm{v}}} = F_{11R} = z + \Lambda \quad F_{22R} = z - \Lambda \quad F_{12R} = F_{21R} = -\left(z - \Lambda^2\right)^{1/2} \\
&H_{11qD\Lambda e/f} = \frac{1}{2}q_{D\mathrm{v}}\left[\left(F_{q\Lambda e/f}F_R\right)_{11} + \left(F_RF_{q\Lambda e/f}\right)_{11}\right] \\
&\qquad = q_{D\mathrm{v}}\left(F_{11q\Lambda e/f}F_{11R} + F_{12q\Lambda e/f}F_{21R}\right) \\
&\qquad = q_{D\mathrm{v}}\left[\mp\frac{1}{2}\sqrt{z}(z+1)\mp\frac{1}{2}\sqrt{z(z-1)}(z-1)^{1/2}\right] \\
&\qquad = \mp\frac{1}{2}q_{D\mathrm{v}}\sqrt{z}[(z+1) + (z-1)] \\
&H_{11pD\Lambda e/f} = \frac{1}{2}p_{D\mathrm{v}}\left[\left(F_{p\Lambda e/f}F_R\right)_{11} + \left(F_RF_{p\Lambda e/f}\right)_{11}\right] = p_{D\mathrm{v}}F_{11q\Lambda e/f}F_{11R} \\
&\qquad = p_{D\mathrm{v}}\left[\mp\frac{1}{2}\sqrt{z}(z+1)\right] = \mp\frac{1}{2}p_{D\mathrm{v}}\sqrt{z}(z+1) \\
&H_{12qD\Lambda e/f} = \frac{1}{2}q_{D\mathrm{v}}\left[\left(F_{q\Lambda e/f}F_R\right)_{12} + \left(F_RF_{q\Lambda e/f}\right)_{12}\right] \\
&\qquad = \frac{1}{2}q_{D\mathrm{v}}\left(F_{11q\Lambda e/f}F_{12R} + F_{12q\Lambda e/f}F_{22R} + F_{11R}F_{12q\Lambda e/f}\right) \\
&\qquad = \frac{1}{2}q_{D\mathrm{v}}\left[\pm\sqrt{z(z-1)} \pm \frac{1}{2}\sqrt{z(z-1)}(z-1) \pm \frac{1}{2}\sqrt{z(z-1)}(z+1)\right] \\
&\qquad = \pm\frac{1}{2}q_{D\mathrm{v}}\sqrt{z(z-1)}(1+z) \\
&H_{12pD\Lambda e/f} = \frac{1}{2}p_{D\mathrm{v}}\left[\left(F_{p\Lambda e/f}F_R\right)_{12} + \left(F_RF_{p\Lambda e/f}\right)_{12}\right] \\
&\qquad = p_{D\mathrm{v}}F_{11p\Lambda e/f}F_{12R} = \pm\frac{1}{4}p_{D\mathrm{v}}\sqrt{z(z-1)} \\
&H_{22qD\Lambda e/f} = \frac{1}{2}q_{D\mathrm{v}}\left[\left(F_{p\Lambda e/f}F_R\right)_{22} + \left(F_RF_{p\Lambda e/f}\right)_{22}\right] = q_{D\mathrm{v}}F_{21q\Lambda e/f}F_{12R} \\
&\qquad = q_{D\mathrm{v}}\left[\mp\frac{1}{2}\sqrt{z}(z-1)\right] = \mp\frac{1}{2}q_{D\mathrm{v}}\sqrt{z}(z-1).
\end{aligned}
\tag{A6.7}
$$

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A6.2 Triplet Electronic Levels

Rotational Energy: First-Order Correction for Centrifugal Distortion

$$\frac{H_{11R}}{B_v} = F_{11R} = x + 2\Lambda,\ F_{22R} = x + 2,\ F_{33R} = x - 2\Lambda$$
$$F_{12R} = -[2x - 2\Lambda(\Lambda - 1)]^{1/2},\ F_{23R} = -[2x - 2\Lambda(\Lambda + 1)]^{1/2},\ F_{13R} = 0$$

$$\begin{aligned} H_{11CD} &= -D_v[F_{11R}F_{11R} + F_{12R}F_{21R}] = -D_v\left[(x + 2\Lambda)^2 + 2x - 2\Lambda(\Lambda - 1)\right] \\ &= -D_v\left[x^2 + 4\Lambda x + 4\Lambda^2 + 2x - 2\Lambda(\Lambda - 1)\right] \\ &= -D_v\left[x^2 + (4\Lambda + 2)x + 2\Lambda^2 + 2\Lambda\right] \end{aligned}$$

$$\begin{aligned} H_{22CD} &= -D_v(F_{22R}F_{22R} + F_{21R}F_{12R} + F_{32R}F_{32R}) \\ &= -D_v\Big[(x + 2)^2 + 2x - 2\Lambda(\Lambda - 1) \\ &\quad + 2x - 2\Lambda(\Lambda + 1)\Big] = -D_v\left[x^2 + 8x + 4 - 4\Lambda^2\right] \end{aligned}$$

$$\begin{aligned} H_{33CD} &= -D_v(F_{33R}F_{33R} + F_{32R}F_{23R}) = -D_v\left[(x - 2\Lambda)^2 + 2x - 2\Lambda(\Lambda + 1)\right] \\ &= -D_v\left[x^2 + (-4\Lambda + 2)x + 2\Lambda^2 - 2\Lambda\right] \end{aligned}$$

$$\begin{aligned} H_{12CD} &= -D_v(F_{11R}F_{22R} + F_{12R}F_{22R}) = D_v\sqrt{2x - 2\Lambda(\Lambda - 1)}[x + 2\Lambda + x + 2] \\ &= 2D_v\sqrt{2x - 2\Lambda(\Lambda - 1)}[x + (\Lambda + 1)] \end{aligned}$$

$$\begin{aligned} H_{23CD} &= -D_v(F_{22R}F_{23R} + F_{23R}F_{33R}) = D_v\sqrt{2x - 2\Lambda(\Lambda + 1)}[x + 2 + x - 2\Lambda] \\ &= 2D_v\sqrt{2x - 2\Lambda(\Lambda + 1)}[x - (\Lambda - 1)] \end{aligned}$$

$$\begin{aligned} H_{13CD} &= -D_vF_{12R}F_{23R} = -D_v\sqrt{2x - 2\Lambda(\Lambda + 1)}\sqrt{2x - 2\Lambda(\Lambda - 1)} \\ &= -2D_v\sqrt{x^2 - 2x\Lambda^2 + \Lambda^2\left(\Lambda^2 - 1\right)}. \end{aligned}$$

(A6.8)

Rotational Energy: Second-Order Correction for Centrifugal Distortion

$$\frac{H_{11R}}{B_v} = F_{11R} = x + 2\Lambda,\ F_{22R} = x + 2,\ F_{33R} = x - 2\Lambda$$
$$F_{12R} = -\sqrt{2x - 2\Lambda(\Lambda - 1)},\ F_{23R} = -\sqrt{2x - 2\Lambda(\Lambda + 1)},\ F_{13R} = 0$$
$$\frac{H_{11CD}}{-D_v} = F_{11CD} = x^2 + (4\Lambda + 2)x + 2\Lambda(\Lambda + 1),\ F_{22CD} = x^2 + 8x + 4\left(1 - \Lambda^2\right),$$

$$F_{33CD} = x^2 + (-4\Lambda + 2)x + 2\Lambda(\Lambda - 1), F_{12CD} = -2\sqrt{2x - 2\Lambda(\Lambda - 1)}[x + \Lambda + 1],$$
$$F_{23R} = -2\sqrt{2x - 2\Lambda(\Lambda + 1)}[x - \Lambda + 1],\ F_{13R} = 2\sqrt{x^2 - 2x\Lambda^2 + \Lambda^2\left(\Lambda^2 - 1\right)}$$

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$$
\begin{aligned}
H_{11CH} &= H_v[F_{11R}F_{11CD} + F_{12R}F_{21CD} + F_{11CD}F_{11R} + F_{12CD}F_{21R}] \\
&= H_v\{(x+2\Lambda)[x^2 + (4\Lambda+2)x + 2\Lambda(\Lambda+1)] \\
&\quad + 2[2x - 2\Lambda(\Lambda-1)][x + (\Lambda+1)]\} \\
&= H_v\{[x^3 + (6\Lambda+2)x^2 + (10\Lambda^2+6\Lambda)x + 4\Lambda^2(\Lambda+1)] \\
&\quad + [4x^2 + x(4+8\Lambda-4\Lambda^2) - 4\Lambda^3 + 4\Lambda]\} \\
&= H_v[x^3 + (6\Lambda+6)x^2 + (6\Lambda^2+14\Lambda+4)x + 4\Lambda^2 + 4\Lambda]
\end{aligned}
$$

$$
\begin{aligned}
H_{22CH} &= H_v(F_{22CD}F_{22R} + F_{21CD}F_{12R} + F_{32CD}F_{32R}) \\
&= H_v\{(x+2)[x^2 + 8x + 4(1-\Lambda^2)] + 2[2x - 2\Lambda(\Lambda-1)][x + \Lambda + 1] \\
&\quad + 2[2x - 2\Lambda(\Lambda+1)][x - \Lambda + 1] \\
&= H_v\{[x^3 + 10x^2 + (-4\Lambda^2+20)x - 8\Lambda^2 + 8] \\
&\quad + [4x^2 + x(4+8\Lambda-4\Lambda^2) - 4\Lambda^3 + 4\Lambda] \\
&\quad + [4x^2 + x(4-8\Lambda-4\Lambda^2) + 4\Lambda^3 - 4\Lambda]\} \\
&= H_v[x^3 + 18x^2 + (-12\Lambda^2+28)x - 8\Lambda^2 + 8]
\end{aligned}
$$

$$
\begin{aligned}
H_{33CH} &= H_v[F_{33CD}F_{33R} + F_{32R}F_{23CD}] \\
&= H_v\{(x-2\Lambda)[x^2 + (-4\Lambda+2)x + 2\Lambda(\Lambda-1)] \\
&\quad + 2[2x - 2\Lambda(\Lambda+1)][x - (\Lambda-1)]\} \\
&= H_v\{[x^3 + (-6\Lambda+2)x^2 + (10\Lambda^2-6\Lambda)x - 4\Lambda^2(\Lambda-1)] \\
&\quad + [4x^2 + (-4\Lambda^2-8\Lambda+4)x + 4\Lambda^3 - 4\Lambda]\} \\
&= H_v[x^3 + (-6\Lambda+6)x^2 + (6\Lambda^2-14\Lambda+4)x]
\end{aligned}
$$

$$
\begin{aligned}
H_{12CH} &= \frac{1}{2}H_v(F_{12CD}F_{22R} + F_{11R}F_{12CD} + F_{12R}F_{22CD} + F_{11CD}F_{12R}) \\
&= H_v\Big\{-4\sqrt{2x - 2\Lambda(\Lambda-1)}[x + (\Lambda+1)]^2 \\
&\quad - \sqrt{2x - 2\Lambda(\Lambda-1)}[2x^2 + (4\Lambda+10)x - 2\Lambda^2 + 2\Lambda + 4]\Big] \\
&= -\frac{1}{2}H_v\sqrt{2x - 2\Lambda(\Lambda-1)}[6x^2 + (12\Lambda+18)x + 2\Lambda^2 + 10\Lambda + 8] \\
&= -H_v\sqrt{2x - 2\Lambda(\Lambda-1)}[3x^2 + (6\Lambda+9)x + \Lambda^2 + 5\Lambda + 4]
\end{aligned}
$$

$$
\begin{aligned}
H_{23CH} &= \frac{1}{2}H_v(F_{23CD}F_{33R} + F_{22R}F_{23CD} + F_{23R}F_{33CD} + F_{22CD}F_{23R}) \\
&= \frac{1}{2}H_v\Big\{-4\sqrt{2x - 2\Lambda(\Lambda+1)}[x - (\Lambda-1)]^2 \\
&\quad - \sqrt{2x - 2\Lambda(\Lambda+1)}[2x^2 + (-4\Lambda+10)x - 2\Lambda^2 - 2\Lambda + 4]\Big] \\
&= -\frac{1}{2}H_v\sqrt{2x - 2\Lambda(\Lambda+1)}[6x^2 + (-12\Lambda+18)x + 2\Lambda^2 - 10\Lambda + 8] \\
&= -H_v\sqrt{2x - 2\Lambda(\Lambda+1)}[3x^2 + (-6\Lambda+9)x + \Lambda^2 - 5\Lambda + 4]
\end{aligned}
$$

$$
\begin{aligned}
H_{13CH} &= \frac{1}{2}H_v(F_{13CD}F_{33R} + F_{11R}F_{13CD} + F_{12R}F_{23CD} + F_{12CD}F_{23R}) \\
&= \frac{1}{2}H_v\Big\{4x\sqrt{x^2 - 2x\Lambda^2 + \Lambda^2(\Lambda^2-1)} + 2\sqrt{2x - 2\Lambda(\Lambda-1)}\sqrt{2x - 2\Lambda(\Lambda+1)}[2x+2]\Big\} \\
&= H_v\sqrt{x^2 - 2x\Lambda^2 + \Lambda^2(\Lambda^2-1)}(6x+4).
\end{aligned}
\tag{A6.9}
$$

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$$\frac{H_{11R}}{B_v} = F_{11R} = x + 2\Lambda,\ F_{22R} = x + 2,\ F_{33R} = x - 2\Lambda$$
$$F_{12R} = -\sqrt{2x - 2\Lambda(\Lambda - 1)},\ F_{23R} = -\sqrt{2x - 2\Lambda(\Lambda + 1)},\ F_{13R} = 0$$
$$\frac{H_{11SR}}{\gamma_v} = F_{11SR} = -(\Lambda + 1),\ F_{22SR} = -2,\ F_{33SR} = (\Lambda - 1),$$
$$F_{12SR} = \frac{1}{2}\sqrt{2x - 2\Lambda(\Lambda - 1)},\ F_{23SR} = \frac{1}{2}\sqrt{2x - 2\Lambda(\Lambda + 1)},\ F_{13SR} = 0$$

$$H_{11SRD} = \gamma_{Dv}(F_{11SR}F_{11R} + F_{12SR}F_{21R}) = \gamma_{Dv}[-(\Lambda + 1)(x + 2\Lambda) - x + \Lambda(\Lambda - 1)] = -\left[(\Lambda + 2)x + \Lambda^2 + 3\Lambda\right]$$

$$H_{22SRD} = \gamma_{Dv}(F_{22SR}F_{22R} + F_{21SR}F_{12R} + F_{23SR}F_{32R}) = \gamma_{Dv}[-2x - 4 - x + \Lambda(\Lambda - 1) - x + \Lambda(\Lambda + 1)] = -\left[4x - 2\Lambda^2 + 4\right]$$

$$H_{33SRD} = \gamma_{Dv}(F_{33SR}F_{33R} + F_{32SR}F_{23R}) = \gamma_{Dv}[(\Lambda - 1)(x - 2\Lambda) - x + \Lambda(\Lambda + 1)] = \left[(\Lambda - 2)x - \Lambda^2 + 3\Lambda\right]$$

$$H_{12SRD} = \frac{1}{2}\gamma_{Dv}(F_{11SR}F_{12R} + F_{12R}F_{22SR} + F_{11R}F_{12SR} + F_{12SR}F_{22R}) = \frac{1}{2}\gamma_{Dv}\sqrt{2x - 2\Lambda(\Lambda - 1)}[(\Lambda + 1) + 2 + x + (\Lambda + 1)] = \frac{1}{2}\gamma_{Dv}\sqrt{2x - 2\Lambda(\Lambda - 1)}[x + 2\Lambda + 4]$$

$$H_{23SRD} = \frac{1}{2}\gamma_{Dv}(F_{22SR}F_{23R} + F_{23R}F_{33SR} + F_{22R}F_{23SR} + F_{23SR}F_{33R}) = \frac{1}{2}\gamma_{Dv}\sqrt{2x - 2\Lambda(\Lambda + 1)}[-\Lambda + 3 + x - (\Lambda - 1)] = \frac{1}{2}\gamma_{Dv}\sqrt{2x - 2\Lambda(\Lambda + 1)}[x + 4 - 2\Lambda]$$

$$H_{13SRD} = \frac{1}{2}\gamma_{Dv}(F_{12SR}F_{23R} + F_{12R}F_{23SR}) = -\gamma_{Dv}\sqrt{[x - \Lambda(\Lambda + 1)][x - \Lambda(\Lambda - 1)]}.$$

(A6.10)

Spin–Spin Interaction: First-Order Correction for Centrifugal Distortion

$$\frac{H_{11R}}{B_v} = F_{11R} = x + 2\Lambda,\ F_{22R} = x + 2,\ F_{33R} = x - 2\Lambda$$
$$F_{12R} = -\sqrt{2x - 2\Lambda(\Lambda - 1)},\ F_{23R} = -\sqrt{2x - 2\Lambda(\Lambda + 1)},\ F_{13R} = 0$$
$$\frac{H_{11SS}}{\lambda_v} = F_{11SS} = 2/3,\ F_{22SS} = -4/3\ F_{33SS} = 2/3, F_{12SS} = 0,\ F_{23SS} = 0,\ F_{13SS} = 0$$
$$H_{11SSD} = \gamma_{Dv}(F_{11SS}F_{11R}) = \lambda_{Dv}[2(x + 2\Lambda)/3]$$
$$H_{22SSD} = \lambda_{Dv}(F_{22SS}F_{22R}) = \lambda_{Dv}[-4(x + 2)/3]$$
$$H_{33SSD} = \lambda_{Dv}(F_{33SS}F_{33R}) = \lambda_{Dv}[2(x - 2\Lambda)/3]$$

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$$
\begin{aligned}
H_{12SSD} &= \frac{1}{2}\lambda_{Dv}(F_{11SS}F_{12R} + F_{12R}F_{22SS} + F_{11R}F_{12SS} + F_{12SS}F_{22R}) \\
&= -\frac{1}{2}\lambda_{Dv}\sqrt{2x - 2\Lambda(\Lambda - 1)}[2/3 - 4/3] = \lambda_{Dv}\sqrt{2x - 2\Lambda(\Lambda - 1)}/3 \\
H_{23SSD} &= \frac{1}{2}\lambda_{Dv}(F_{22SS}F_{23R} + F_{23R}F_{33SS} + F_{22R}F_{23SS} + F_{23SS}F_{33R}) \\
&= \frac{1}{2}\lambda_{Dv}\sqrt{2x - 2\Lambda(\Lambda + 1)}[-4/3 + 2/3] = \lambda_{Dv}\sqrt{2x - 2\Lambda(\Lambda + 1)}/3 \\
H_{13SSD} &= \frac{1}{2}\lambda_{Dv}(F_{13SS}F_{33R} + F_{13R}F_{33SS} + F_{12SR}F_{23R} + F_{12R}F_{23SR}) = 0.
\end{aligned}
\tag{A6.11}
$$

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